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Preparation of Optically Transparent Films of Poly(methyl methacrylate) (PMMA) and Montmorillonite

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ABSTRACT

Transparent polymeric material with enhanced thermal, mechanical and barrier properties are of special interest for advanced structural, optical and photonic applications. The present paper reports a novel solution processing scheme for fabricating optically transparent polymer nanocomposites involving organophilic layered silicates. It is shown that the nanocomposite material prepared with PMMA and an organically modified montmorrilonite maintains the excellent optical transparency of PMMA. Small-angle x-ray scattering of the polymer nanocomposite material does not show any Bragg's reflection of the organophilic layered silicate. The optical transparency of the nanocomposite material is attributed to a high degree of exfoliation of the montmorrilonite in the polymer matrix.

INTRODUCTION

Organic and inorganic fillers are commonly used to enhance polymer performance. Among the various inorganic fillers, nanoscale layered silicates, which have a sheet-like structure and an extremely large surface area ($700 \text{ m}^2/\text{g}$ vs. $150 \text{ m}^2/\text{g}$ for carbon black) [1], are especially attractive for conferring thermal, mechanical and barrier properties to polymeric materials for specific applications. The organic affinity of the nanophase fillers can be modified by cation exchange with organic salts to tailor the structure and properties of the resulting polymer composite material. Individual platelets of nanoscale layered silicates have a length scale smaller than the wavelength of visible light. As a result, they may be used to reinforce organic polymers such as PMMA and polycarbonate without significantly degrading their optical clarity. The transparent polymer nanocomposite material has potential for advanced applications in protective coatings, windows, and integrated optical devices [2].

In order to achieve the maximum reinforcement of the layered silicates, their unit layers must be uniformly dispersed in the polymer matrix and have strong interaction with the polymer [3]. Various methods, such as solution mixing [4,5], melt mixing [6,7], and in-situ polymerization [8,9], have been used to disperse layered silicates into organic polymers. However, except a very few cases [9,10], results are usually a composite material containing both intercalated and exfoliated layered silicates. Normally, such a phase-separated composite material does not lead to significant improvement in thermal, mechanical and barrier properties over its host polymer. The only system that exhibits dramatic property improvement is the nylon 6-montmorrilonite nanocomposites obtained by in-situ polymerization. This composite material contains highly exfoliated montmorrilonite unit layers that are uniformly dispersed in the polymer matrix. As the in-situ polymerization of nylon 6 from caprolactam is initiated by the amino acid counter ions on the surface of the montmorrilonite, it is believed that the interfacial nylon molecules are tethered to the layered silicate through the organic salt.

In the present study, a novel solution processing scheme is devised to produce optically transparent PMMA-montmorrilonite nanocomposites. The nanodispersion of an organically modified montmorrilonite (OMM) in PMMA is achieved by mixing in a common solvent with ultrasonic agitation. The composite solution is sprayed into a fine mist to result in a rapid removal of the solvent and thereby, to obtain the nanodispersion of the OMM in the polymer matrix. The x-ray scattering patterns and optical transmission spectra of the sprayed polymer composite films are compared with those obtained from the composite films prepared by the conventional solution casting method.

EXPERIMENTAL

Materials

The OMM used in this study is Cloisite 6A (C6A) from Southern Clay products, Inc. This montmorrilonite is cation-exchanged with 1.40 meq/g of dimethyl dehydrogenated tallow ammonium from a sodium montmorillonite, Cloisite Na^+ (CNa). Since the cation-exchange capacity of CNa is $0.92 - 0.95$ meq/g, therefore the C6A unit layers are covered with about 50% excess of the surfactant. The characteristic d-spacing of C6A is 36.4 Å. The PMMA was obtained from Scientific Polymer Products. It has a weight-average molecular weight of 63,000 g/mol and a polydispersity of 1.7. The solvent used is xylene from Aldrich Chemicals.

Sample Preparation

In this study, composite solutions of PMMA and C6A were prepared by adding PMMA to a 2% C6A solution in xylene. The final solutions had a concentration of approximately 12 wt% solid content. Two mixing methods, i.e., mechanical stirring and ultrasonic agitation, were applied to preparing the solutions and the detailed processing conditions are provided in Table 1. The ultrasonic agitation vessel was immersed in an ice water bath to control the temperature. The solutions were immediately used after mixing for preparing the polymer composite films by a spraying or a casting method. The spraying was carried out using a Paasche single action-gravity feed airbrush with a 0.635mm diameter nozzle under a pressure of 20 psi. The films were sprayed on a glass substrate from a distance of 15 cm. The various polymer composite samples prepared are denoted by their solution preparation and film forming methods. For example, a D-C film indicates the sample prepared from solution D, followed by the solution casting method. All the polymer composite films characterized had been vacuum dried at 80°C overnight.

Characterization

Small-angle x-ray scattering (SAXS) was used to probe the dispersion of C6A in the polymer composites. It was performed using an Ultrax 18 rotating anode generator equipped with a Statton camera. CuK_α radiation ($\lambda = 1.5418$ Å) with a graphite monochromator was used at an accelerating voltage of 50kV/150mA. The x-ray scattering patterns were recorded on phosphor image plates. UV-visible spectra of the polymer composite films were measured over a wavelength range from 200 to 1000 nm with a Hewlett Packard 8453 spectrophotometer at ambient conditions.

Table 1. Composite solution preparation conditions

| Solution	C6A/xylene	PMMA/C6A/xylene
A	Mechanical stirring/1 hr	Mechanical stirring/1 hr
B	Mechanical/1 hr + Ultrasonic/3 hrs	Mechanical stirring/1 hr
C	Mechanical/1 hr + Ultrasonic/3 hrs	Ultrasonic agitation/1 hr
D	Mechanical/1 hr + Ultrasonic/3 hrs	Ultrasonic agitation/3 hrs
E	Ultrasonic agitation/1 hr	Ultrasonic agitation/1 hr
F	Mechanical stirring/1 hr	Ultrasonic agitation/3 hrs

RESULTS AND DISCUSSION

Small-angle x-ray scattering was used to probe the nanodispersion of C6A in both sprayed and cast composite films. The as received C6A has a d-spacing of 36.4 Å, which decreases to 34Å after C6A is vacuum dried at 80°C. However, after C6A is dissolved in xylene and then vacuum dried at 80°C, it shows a d-spacing of 31.6Å. It suggests that once C6A is dissolved in xylene, some dimethyl dehydrogenated tallow ammonium is removed from the C6A surface resulting in the smaller d-spacing. Figure 1 shows the x-ray scattering pattern of a D-C composite film. The film exhibits a basal spacing of 38.2Å, indicating PMMA molecules have migrated into the C6A gallery and formed an intercalated polymer composite material. The flat-view scattering pattern of the polymer composite suggests that the intercalated C6A platelets are uniformly dispersed in the film, while the edge-view pattern indicates that the C6A platelets are oriented to some degree in the plane of the film, giving rise to stronger scattering intensity in equatorial direction.

(a)   (b)
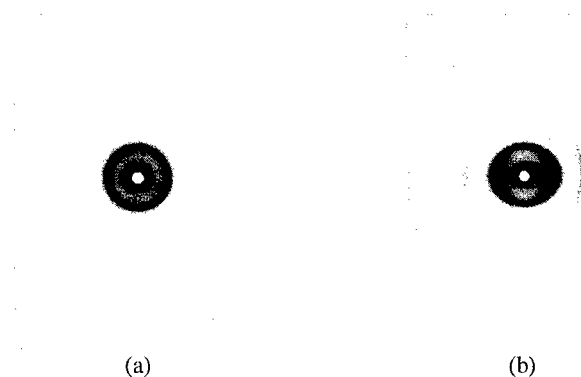
**Figure 1.** X-ray scattering pattern of a D-C composite film: (a) flat-view and (b) edge-view.

The D-S composite film did not show an x-ray scattering pattern of significant intensity in either flat-view or edge-view test configuration. Figure 2 compares the intensity scan in equatorial direction of the flat view scattering pattern of a D-C composite film with that of a D-S composite film. The sprayed composite film shows minimal scattering intensity due to Bragg's reflection from the basal spacing of the layered silicate. It suggests that the OMM was exfoliated

in the D-S composite film. Since the D-C and the D-S composite films were prepared from the same solution, the distinct morphologies of the two films must arise from the different film forming processes. In order to cast optically clear and surface-smooth polymer composite films, solvent evaporation was controlled at a considerably slow rate. Previously, it was found that when the solvent of a polymer composite solution of layered silicates is removed to a certain extent, the solution forms a gel-like structure. This gel-like structure gradually builds up as the layered silicate platelets orient themselves towards a position of minimum free energy under the influence of Brownian motion [11]. Upon coalescing of the platelets, polymer chains are entrapped in between platelets resulting in a basal spacing of 38-40Å. In the sprayed films, the solvent was removed so rapidly that the system did not have an opportunity to reach the equilibrium state. As a result the composite film retained the nanodispersion of the layered silicate platelets in the polymer matrix as that in the composite solution.
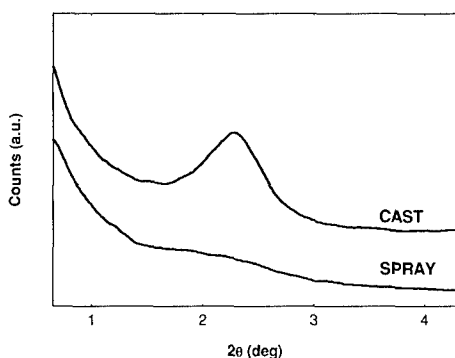

Figure 2. X-ray intensity scan of a sprayed and a cast composite film prepared from solution D (intensity vertically shifted for clarity).

A series of composite films were prepared by the spray method from the various composite solutions. Their x-ray intensity scan in equatorial direction of the flat-view scattering pattern is shown in Figure 3. It indicates that A-S composite film sprayed from solution A had the characteristic basal reflection of intercalated structure. Since the same spray method was used to prepare A-S as well as D-S composite film, the difference in the morphology must originated from their composite solutions. This points out that mechanical stirring alone is insufficient to exfoliate C6A into individual unit layers in the composite solution. The films that showed the highest decrease in the degree of coherent layer stacking were those sprayed from solutions D and F, which had experienced the longest ultrasonic agitation after the addition of the layered silicate. The initial ultrasonic agitation of C6A/xylene solution did not seem to facilitate the subsequent exfoliation of the layered silicate in the composite solution, which may be due to a poor chemical affinity between PMMA and C6A. When the composite solution is under ultrasonic agitation, high intensity energy is introduced into the solution keeping the layered silicate platelets in constant motion and dissociated from one another. The lack of basal reflection in D-S composite film pattern suggests that using ultrasonic agitation to disperse layered silicates in polymer solutions achieves exfoliation even when the silicate concentration is moderately high (20% wt).
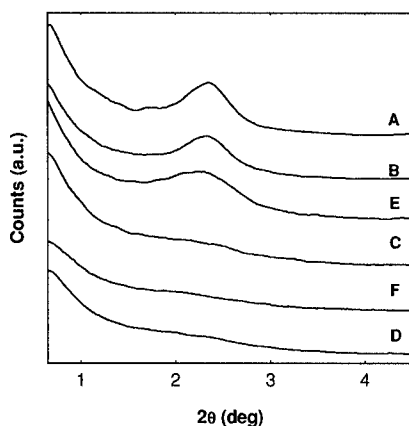
Figure 3. X-ray intensity scan of various sprayed composite films (vertically shifted for clarity).

The optical transmittance of several sprayed and cast composite films is shown in Figure 4. The transmittance was measured with a UV-Vis spectrometer over a wavelength range from 200 to 1000 nm. Figure 4 shows that the most optically clear composite films have a transmission between 80 and 90% in the visible light region. However, the optical transmission of the cast composite films was relatively poor, especially in the low wavelength region. This indicates that the cast films contain layered silicate particles that are large enough to scatter the visible light. The result suggests that the present processing scheme may open new windows for achieving nanodispersion of layered silicates in organic polymers, even when the polymer is incompatible with the layered silicate.
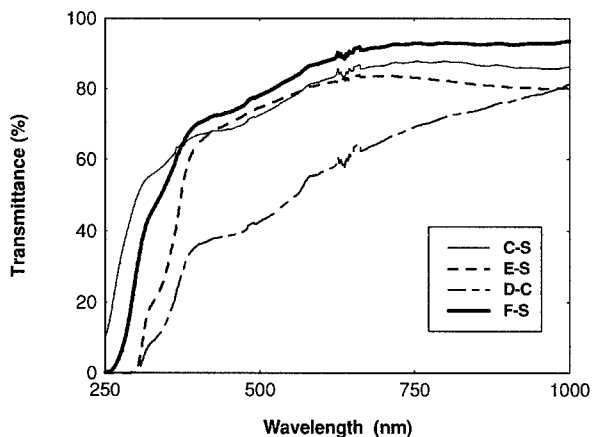
Figure 4. Optical transmittance of sprayed and cast PMMA/C6A composite films.

CONCLUSIONS

A novel solution processing scheme was devised to produce optically transparent polymer nanocomposites of layered silicates. In the processing scheme, ultrasonic agitation is utilized to achieve nanodispersion of an organophilic layered silicate in the composite solution of a choice polymer. Then the solvent is rapidly removed by spraying the composite solution into a fine mist. This rapid solvent removal greatly curtails the phase separation kinetics of the layered silicates, even though it may be thermodynamically favored. It is shown that PMMA/C6A nanocomposites (20 wt% of the layered silicate) prepared by the present processing scheme have an optical transmission greater than 80% in the visible light region. This processing scheme opens new processing windows for achieving polymer/layered silicate nanocomposites even if the polymer may not be compatible with the layered silicate.

ACKNOWLEDGMENTS

REFERENCES

1. Olphen, H. V. *An introduction to clay colloids chemistry*; Wiley: New York, 1977.
2. Carotenuto, G.; Nicolais, L.; Kuang, X. *Appl. Composite Matls.* **1996**, *3*, 103-116.
3. LeBaron, P. C.; Wang, Z.; Pinnavaia, T. J. *Appl. Clay Sci.* **1999**, *15*, 11-29.
4. Gao, Z.; Xie, W.; Hwu, J. M.; Wells, L.; Pan, W.-P. *J. Thermal Anal. Calorim.* **2001**, *64*, 467- 475.
5. Lemmon, J. P.; Wu, J.; Oriakhi, C.; M.Lerner, M. *Electrochimica Acta* **1995**, *40*, 2245-2249.
6. Alexandre, M.; Beyer, G.; Henrist, C.; Cloots, R.; Rulmont, A.; Jérôme, R.; Dubois, P. *Macromol. Rapid Commun.* **2001**, *22*, 643-646.
7. Vaia, R. A.; Jandt, K. D.; Kramer, E. J.; Giannelis, E. P. *Chem. Mater.* **1996**, *8*, 2628-2635.
8. Messersmith, P. B.; Giannelis, E. P. *Chem. Mater.* **1994**, *6*, 1719-1725.
9. Lincoln, D. M.; Vaia, R. A.; Wang, Z.-G.; Hsiao, B. S. *Polymer* **2001**, *42*, 1621-1631.
10. Chen, G.; Ma, Y.; Qi, Z. *Scripta Materialia* **2001**, *44*, 125-128.
11. Luckham, P. F.; Rossi, S. *Adv. Colloid Interface Sci.* **1999**, *82*, 43-92.